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Competition between Na_2SO_4 and Na sulfide in the upper crust of Io

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Abstract. The Na atmosphere of Io requires a Na-S-O phase in the outer surface layers. Considering the various mechanisms for extraction of Na to the surface, the possible primary phases are Na_2O, Na_2S_x, and Na_2SO_4. However, regardless of the primary phases brought to the surface, the shallow crustal recycling of material implied by the ongoing volcanism will tend to produce thermochemical equilibrium and cause all Na to end up as Na_2SO_4 or Na_2S_x. This hypothesis is investigated by relatively model-independent thermodynamic calculations. The major assumption is that material is statistically circulated to sufficiently high temperatures by burial that thermochemical equilibrium can be attained. For a wide range of assumed crustal (PT) conditions, Na_2O will be converted to Na_2SO_4. During residence in the shallowest crustal regions dominated by liquid SO_2, e.g., SO_2 geysers or fumaroles, or for any crustal regimes where SO_2 and S are in comparable abundances, Na-sulfides will be converted to Na_2SO_4. However, in high-temperature, low-pressure regimes with a low relative abundance of SO_2 relative to S (e.g., due to outgasing of SO_2), Na_2SO_4 is converted to Na sulfides. Such regimes could be relatively common on Io, e.g., associated with flows, lava lakes, or shallow intrusions. Consequently, because of thermochemical equilibration in different crustal environments, both Na_2SO_4 and Na sulfides will coexist on the Io surface.

Introduction

Relatively little is known about formation mechanisms for planetary Na atmospheres. In the case of Io it is widely accepted that Na is removed from the outer surface layers by sputtering with magnetospheric ions [e.g., *Johnson and Matson*, 1989; *Cheng and Johnson*, 1989]. The Io Na cloud is most easily understood if sputtering occurs from surface materials as opposed to atmospheric constituents. The spectra of the magnetospheric ions show only O, S, and Na, which has been interpreted by most workers [e.g., *Johnson and Burnett*, 1990, 1993] as indicating that atmospheric Na arises from Na-S-O surface phases and that negligible Na is contained in silicate phases. Relative to Na, significant upper limits for Si in the Io torus have been reported for the most probable states of ionization [*McGrath*, 1993].

Four plausible hypotheses for the nature and origin of the Na-bearing phases have been suggested. (1) The Na is indicative of evaporite deposits which are residues of ancient Ionian oceans [*Fanale et al.*, 1974; *Nash and Fanale*, 1977; *Kargel*, 1993]. Terrestrial analogies would suggest sulfate and halide salts, but the high chloride/sulfate ratio for terrestrial oceans is primarily a consequence of biological reduction of sulfate [*Schlesinger*, 1991]. Thus, given the high chondritic S/Cl, a predominance of sulfates would be expected for Ionian oceans. (2) The Na was thermally evaporated from molten silicate during volcanic eruptions as Na atoms [*Fanale et al.*, 1982]. (3) The Na was extracted from silicate materials as Na-sulfides by elemental S [*Lunine and Stevenson*, 1985; *Johnson and Burnett*, 1990; also G. R. VanHecke and D. B. Nash, unpublished manuscript, 1984]. (4) Na-rich sulfates were produced by interaction of SO_2 with silicate materials [*Johnson and Burnett*, 1993; G. R. VanHecke and D. B. Nash, unpublished manuscript, 1984].

The question investigated in this study is, regardless which of the above primary source mechanisms (1-4) predominates, what would be the stable Na-bearing phases if thermochemical equilibrium is established during recycling within the upper crustal layers on Io? Taking rapid crustal recycling on Io as established [e.g., *Veeder et al.*, 1994], three basic assumptions are made.

1. SO_2 and elemental S are the dominant surface compounds, in excess compared with any Na-bearing phase. I am essentially adopting the Io model of *Smith et al.* [1979] or *Kieffer* [1982] with an upper crust which is composed almost entirely of S-SO_2 and through which volatiles are rapidly recycled. The regions beneath the upper crust are predominantly silicate, but I assume that the upper crust contains only minor amounts of silicate in the form of occasional magmatic intrusions. SO_2 is a documented surface constituent [e.g., *Lellouch et al*, 1990]; elemental S is not but is assumed to be present by most workers [e.g., *Moses and Nash*, 1991].

2. Crustal recycling buries the phases produced by all of the four primary mechanisms (1-4) to sufficiently high crustal temperatures that thermochemical equilibrium can be obtained. This assumption is crucial because, for ~125-140 K surface temperatures [e.g., *Johnson and Matson*, 1989], thermochemical reaction times are likely to be long, even relative to geologic time. A detailed model of the recycling has been worked out by *Kieffer* [1982] in which both S and SO_2 are carried to sufficient crustal depth to be the source of the observed fumaroles (SO_2?) and volcanoes (S?) [*McEwen and Soderblom*, 1983]. Thermochemical equilibrium need not be achieved on every cycle; it is sufficient that it be achieved statistically over geologic time. Given the essentially inexhaustible nature of tidal heating, it is reasonable to assume that the present crustal conditions on Io have been in place for at least 10^9 years, far longer than for any specific geothermal region in the outer

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kilometer of the Earth. However, because it cannot be proved that thermochemical equilibrium is acquired rapidly, it is necessary to assume:

3. During residence in the outer micron of the surface, radiation chemical processes do not significantly alter the products of thermochemical equilibrium. Because of the recycling all upper crustal materials will periodically be transiently exposed to surface irradiation. Here radiation chemistry would include the effects of solar ultraviolet photons, magnetospheric electrons, and magnetospheric ions.

For clarity all calculations below are discussed in terms of the most important single reaction leading to the dominant products. Alternative reactions have been systematically considered to determine that this approach is valid. Moreover, the results of several of the calculations have been verified using a sophisticated free energy minimization program incorporating a large thermodynamic data base of Na-S-O compounds [*Sharp*, 1992].

The importance of crustal recycling was previously discussed by *Nash and VanHecke* [1992] with emphasis on the enthalpy changes during recycling. The approach and results of these authors appear consistent with mine.

Calculations

Oxide conversion

Fanale et al. [1982] discuss volcanic outgasing of Na atoms. In the presence of even trace amounts of H, the gas phase species would be NaOH; however it is quite possible that H is much less than Na in the upper crust resulting in a negligible fraction of volatile Na being tied up as NaOH. Regardless of whether Na or NaOH is the volatile species, it is likely that rapid oxidation to NaO by radiation-produced O species would occur even at the low surface temperatures. It is not possible to evaluate the fate of chemisorbed NaO on surfaces precisely, but eventually NaO will be converted to Na_2O or to sulfide if adsorbed onto an elemental S grain. Even if photochemically mediated grain surface reactions are not effective, thermochemical conversion of the NaO radical upon burial should be rapid, with the products being either Na_2O, Na_2SO_4, or Na sulfides. The fate of Na_2SO_4 and Na sulfides is discussed below. Here we consider the destruction of Na_2O on burial to produce Na_2SO_4. Although a variety of reaction mechanisms are possible, all pathways that we have considered (e.g., through Na_2SO_3) can be summarized schematically by the reaction

$$2Na_2O + 3SO_2 = S + 2Na_2SO_4 \quad (1)$$

Na_2O is solid throughout the relevant (PT) regions. The melting point of Na_2SO_4 is 1157 K. Liquid immiscibility with S is assumed; thus Na_2SO_4 has been taken as a pure phase for all calculations.

As discussed below, thermodynamic calculations show that for the whole range of plausible (PT) conditions for the outer few kilometers of Io, reaction (1) proceeds in the direction as written. The alternative Na_2O destruction reaction leading to Na sulfide formation is also effective. The competition between Na_2SO_4 and Na sulfides is discussed below.

Realistically, the crust of Io is a very complex, thermally heterogeneous region. Thus, rather than adopt an assumed temperature gradient (Iotherm), we consider a broad range of (PT) conditions ranging from 0.1 to 100 atm and 200 to 1500 K. This temperature range extends from the minimum temperature (200 K) at which thermochemical reactions might be effective on geologic timescales to silicate magmatic temperatures, the maximum plausible for the Io crust. The 200 K limit also approximately corresponds to the melting point of SO_2. Liquid SO_2 provides a fluid medium to facilitate thermochemical reactions. Although arbitrary, the adopted pressure range corresponds to the outer 2 km, and by analogy with terrestrial hydrology, it is probably unreasonable to consider a compound as volatile as SO_2 to be routinely buried to greater depths than this. As illustrated in Figure 1, it is useful to divide this (PT) space into three regions defined by the gas-liquid phase boundaries of SO_2 and elemental S.

Region I is characterized by the presence of liquid SO_2, and even for Iotherms as high as 1000 K/km, a significant portion of the upper crust would be in the SO_2 liquid field [*Kieffer*, 1982]. S is mainly solid in I, although in the high-P, high-T (>388 K) corner of I, liquid S and liquid SO_2 coexist. For condensed phases, as in region I, the direction of reaction (1) is determined by the Gibbs free energy change (ΔG), which can be calculated from tabulated standard-state free energies and the SO_2 phase diagram. Values in the range of -900 kJoules are obtained for (1), indicating that, in the presence of liquid SO_2 and condensed S, Na_2O would be converted to Na_2SO_4 in region I. There is little uncertainty in this result.

Region II is defined by SO_2 gas (strictly speaking, fluid, as much of region II is above the SO_2 critical temperature) and condensed S (mainly liquid, but solid S in the low-T, low-P portions of region II). Any miscibility of liquid S and SO_2 is neglected. In region II the equilibrium constant for reaction (1) can be related to the equilibrium SO_2 fugacity: $K = 1/f(SO_2)^3$, where the equilibrium SO_2 fugacity is the value where Na_2O and Na_2SO_4 can coexist. K can be calculated from tabulated standard state Gibbs free energies of formation [*Barin*, 1989], yielding equilibrium SO_2 fugacities, as shown in Figure 2. The

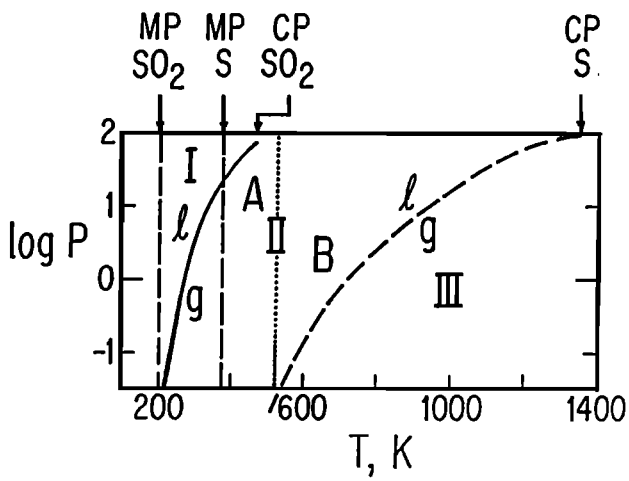

Figure 1. The range of pressure and temperature considered is conveniently divided into three regions based on the vapor pressure curves of SO_2 (solid curve) and elemental S (dashed curve). In region I both SO_2 and S are condensed phases. In region II, SO_2 is a gas, but S remains condensed. Region II is further divided into regions IIA and IIB above and below 525 K, the transition temperature of solid Na_2S_5 to an immiscible Na_2S_x liquid coexisting with liquid S. In region III both SO_2 and S are gases. For reference, the melting points (MP) and critical points (CP) are shown. Pressure variations of the melting points can be neglected.

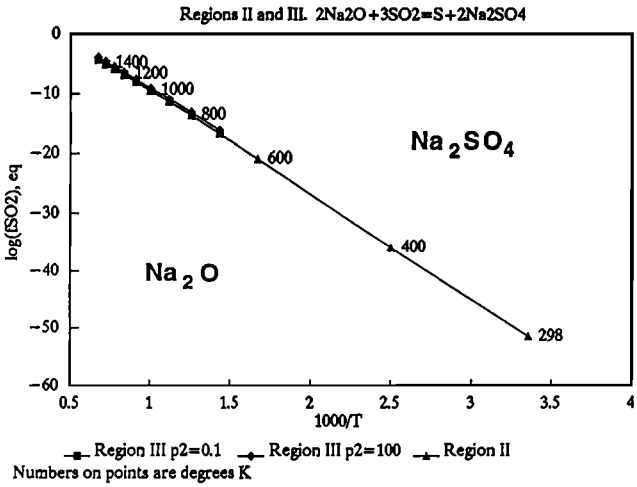

Figure 2. This diagram shows the relative stability fields of Na_2O and Na_2SO_4, coexisting with SO_2 and elemental S. The curve shows the calculated equilibrium SO_2 fugacity (atm) at which Na_2O and Na_2SO_4 can coexist. Na_2SO_4 is the stable phase in the field above the line, and Na_2O is the stable phase in the field below the line. Although calculated for region II, the relationship is a good approximation for region III also, as shown. The estimated daytime SO_2 atmospheric pressure [*Lellouch et al.*, 1990] is 10^{-9} atm. In the SO_2-rich upper crust of Io, SO_2 fugacities should be at least this high, indicating conversion of Na_2O to Na_2SO_4.

curve defines a phase boundary between the stability fields of Na_2SO_4 (lower temperatures and higher SO_2 fugacities) and Na_2O (higher T and low SO_2 fugacities). Estimated fugacity coefficients [*Walas*, 1985] indicate that SO_2 fugacity and pressure differ by much less than a factor of 2 over the (PT) region defined by Figure 1. Thus, Figure 2 shows that the equilibrium SO_2 pressures are quite low over the whole range of temperature in region II, favoring Na_2SO_4 at the expense of Na_2O for a planet such as Io with SO_2 as the dominant volatile.

In region III both SO_2 and S are gases. Gas phase speciation for elemental S is complex, containing a distribution of species S_x, with x ranging from 2 to 8; however, thermodynamic data are available from which the gas phase compositions can be calculated as a function of temperature and pressure [*Chase et al.*, 1985]. At higher temperatures, S_2 is dominant; thus it is logical to write chemical reactions using S_2 as the representative gas phase elemental S species at all temperatures. Thus the equilibrium constant for reaction (1) in region III can be written as $f(S_2)^{1/2}/f(SO_2)^3$. To calculate equilibrium $f(SO_2)$ [or $f(SO_2)/f(S_2)$] , $f(S_2)$ is taken as an independent variable with values of $f(S_2)$ ranging from 0.1 to 100 atmospheres. However, since the equilibrium $f(SO_2)<<f(S_2)$, the changes in log $f(SO_2)$ due to variations in $f(S_2$ are relatively small, and the calculated SO_2 fugacities for region III are close to those for region II, as shown on Figure 2.

In summary, except for crustal regions almost totally depleted in SO_2, Na_2O will be thermochemically converted to Na_2SO_4. The possibility of extreme SO_2 depletion requires further discussion, but this is deferred until the role of Na sulfides is discussed in the following section.

Sulfide-Sulfate Competition

There are a variety of stable Na sulfides of the type Na_2S_x, with x=1, 2, 3, 4, 5. Thermodynamic data are available for x=1-4. Experiments indicate Na_2S_2 as the product of elemental S, silicate reactions [*Johnson and Burnett*, 1990]. However, in the presence of elemental S the Na-S phase diagram [e.g., *Rosen and Tegman*, 1972] shows that Na_2S_5 is the stable phase at low (<525 K) temperature. Thus for region I (Figure 1) with all condensed phases, sulfate-sulfide competition is represented by

$$Na_2S_5(s) + 2SO_2(l) = 6S(c) + Na_2SO_4(s) \quad (2)$$

where s, l, c refer to solid, liquid, and condensed, respectively (c is used for S because a small portion of I is above the S melting point.) Gibbs free energies of formation are not available for Na_2S_5; these have been estimated based on data for Na_2S_x with x=1-4. The adopted values are shown in Table 1. The errors introduced in the calculated ΔG for (2) from these estimates (±5-10 kJ) are not significant.

For region I (Figure 1) with all condensed phases the DG values for (2) are -220 to -320 kJ showing that, with S and liquid SO_2 present, Na_2S_5 is converted to Na_2SO_4 in this region.

In region II above 525 K an immiscible Na_2S-S liquid coexists with liquid S and SO_2 gas; thus region II is divided into regions IIA and IIB, above and below 525 K, respectively (Figure 1).

In region IIA, sulfate-sulfide competition can be described by (2) except that gaseous SO_2 is present; thus the equilibrium constant for reaction (2) can be related to SO_2 fugacity: $K=1/f(SO_2)^2$. Given the fact that SO_2 is a major upper crustal constituent, the resulting equilibrium SO_2 fugacities shown in Figure 3 are low, indicating that Na_2SO_4 is strongly favored in region IIA. For reference the daytime atmospheric SO_2 surface pressure is roughly 10^{-9} atm, and SO_2 pressures in the upper crust should be much higher than this.

Calculation of sulfate-sulfide competition in region IIB requires knowledge of the activities of $Na_2S_x(l)$ components in the immiscible Na_2S-S liquid. These activities cannot be calculated exactly, and this represents the major source of uncertainty in the results of this study. However, based on vapor pressure and cell EMF data, models of the relative proportions of Na_2S_x species (i.e., chain length distributions) have been formulated [*Cleaver and Sime*, 1983; *Tegman*, 1976] as a function of temperature and bulk composition (Na_2S/S) of the Na_2S_x liquid. The present calculations are based on the Cleaver and Sime model C_{23}. Region II is defined by the presence of liquid S, thus the S activity is 1, fixing the Na_2S_x liquid bulk composition as a function of T. The Cleaver-Sime model then gives the mole fractions of all Na_2S_x components. Sulfate-sulfide competition can be evaluated by assuming ideal solid solution of the Na_2S_x components, equating the Na_2S_4 mole fraction to its activity. Any Na_2S_x component can be used to describe sulfate-sulfide competition; Na_2S_4 has been chosen because it is usually a major species and because thermodynamic

Table 1. Estimated Standard Free Energies of Formation of Na_2S_5

T, K	ΔG°_f KJ/mol
300	-415
400	-405
500	-389

Based on data for Na_2S_x with x = 1-4 from *Barin* [1989]

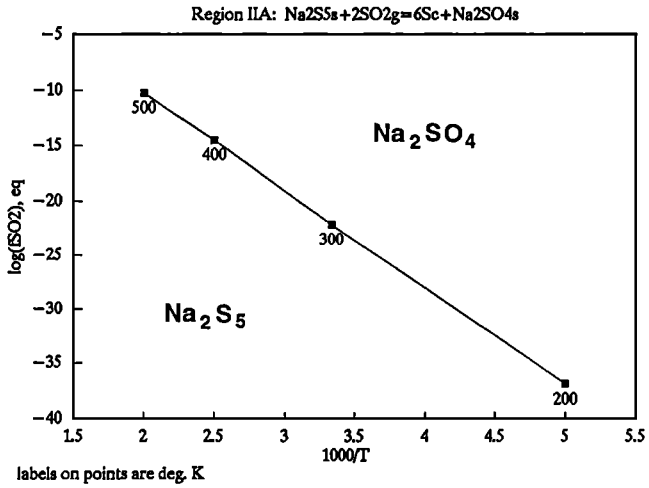

Figure 3. Analogous to Figure 2 for Na_2O, this diagram shows the relative stability fields for Na_2S_5 and Na_2SO_4 for region IIA of Figure 1. The curve shows the calculated equilibrium fugacity where Na_2S_5 and Na_2SO_4 can coexist. Lower temperature regions (below roughly 700 K) favor the formation of Na_2SO_4.

data for pure Na_2S_4 (necessary to calculate the equilibrium constant) are available. Thus in region IIB

$$(Na_2S_4)(l) + 2SO_2(g) = 5S(l) + Na_2SO_4(s) \qquad (3)$$

where the parentheses emphasize that $Na_2S_4(l)$ is a component in a Na_2S_x liquid. For reaction (3) in region IIB the equilibrium constant $K = 1/[X_4 f(SO_2)^2]$, where X_4 is the mole fraction of the $Na_2S_4(l)$ component in the immiscible Na-S liquid. With liquid S present, X_4 is a known function of T only, K can be calculated from the Gibbs free energies of formation of the pure phases, and thus the equilibrium $f(SO_2)$ for region IIB can be calculated as shown in Figure 4.

Region III is defined by the presence of both elemental S and SO_2 in the gas phase. Adopting S_2 as the gas phase species, as discussed in the previous section, the equilibrium constant for reaction (3) is given by log K= (5/2) log $f(S_2)$-2 log $f(SO_2)$-log (X_4). On Io, $f(S_2)$ and $f(SO_2)$ vary independently; thus the equilibrium $f(SO_2)$ has been calculated allowing $f(S_2)$ to range from 0.1 to 100 atm (Figure 4).

The calculations for region III were done using equilibrium S_2 vapor pressure data for Na-S liquids as summarized by *Tegman* [1976]. Taking $p(S_2)$ and T as independent variables, Figure 4 of *Tegman* [1976] was used to obtain the bulk Na_2S/S of the Na_2S_x liquid in equilibrium with the chosen $p(S_2)$. Significant extrapolation of the available data is required to calculate the highest T points shown on Figure 4, and the calculations above 1100 K are much less reliable. Given a T and bulk liquid Na_2S/S, the Cleaver and Simes model was used to calculate X_4. When this X_4, based on a given $p(S_2)$, is combined with the equilibrium constant for (3), it is being somewhat indirectly assumed that $f(S_2)$=$p(S_2$. This assumption introduces some error for the higher (10-100 atm) $p(S_2)$. These errors cannot be assessed, but it is unlikely that the qualitative conclusions of the calculations are affected.

For a constant $f(S_2)$, Figure 4 shows that the equilibrium $f(SO_2)$ decreases with decreasing T until the condensation T for liquid S is reached and the region III and IIB curves intersect. In the higher T portions of both regions IIB and III the $f(SO_2)$ required to stabilize Na_2SO_4 relative to Na_2S_x are relatively high,

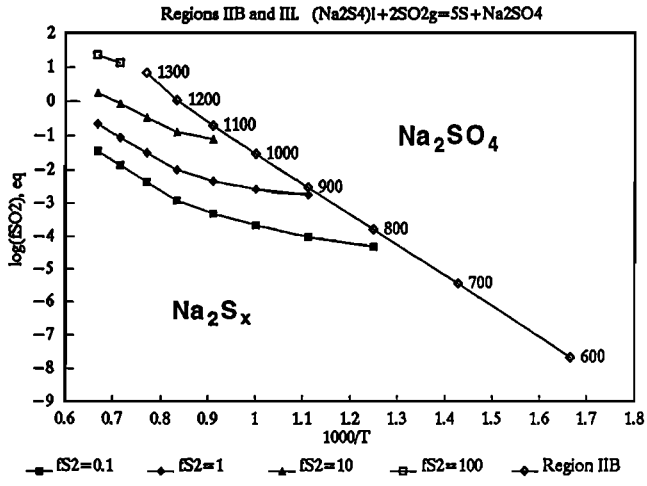

Figure 4. In region IIB the equilibrium SO_2 fugacity where $Na_2S_x(l)$ and Na_2SO_4 coexist can be represented by a single curve. Calculations were done for Na_2S_4 as a representative component of the NA_2S_x liquid. For region III the equilibrium SO_2 fugacities depend on S_2 fugacity as well as temperature. Calculations are shown for different values of $f(S_2)$. At higher temperatures and higher $f(S_2)$ the stability field of $Na_2S_x(l)$ expands relative to Na_2SO_4. Temperature, $f(S_2)$, and $f(SO_2)$ vary independently in the upper crust of Io, and most of the regions in this figure are plausible for Io. For example, in volcanic plumes or S lava lakes where SO_2 venting produces a S-rich, high temperature environment, Na_2S_x will be formed.

so in general, the high-T regions of the Io upper crust favor Na_2S_x.

The implications of the calculations for Io in region III are somewhat easier to evaluate using isothermal plots of $f(S_2)$ vs. $f(SO_2)$. An example for 1100 K is shown in Figure 5. As expected, higher $f(S_2)$ favors Na_2S_x and lower $f(S_2)$ favors Na_2SO_4. In general unless there is essentially complete depletion of SO_2 relative to S, Na_2SO_4 is favored for temperatures less than about 800 K. However, at higher temperatures the stability field of Na_2S_x increases to higher SO_2 fugacities.

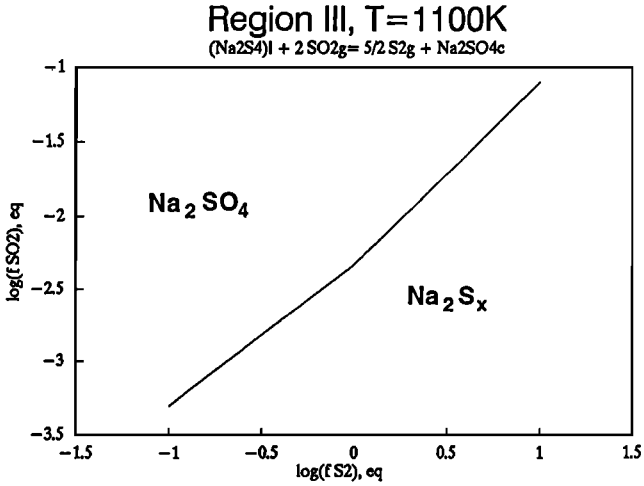

Figure 5. A high temperature isothermal stability field diagram for Na_2SO_4 and $Na_2S_x(l)$. For crustal regions where venting has depleted SO_2 relative to S, Na_2SO_4 can be converted to $Na_2S_x(l)$. If SO_2 can be trapped at high temperatures in regions of high crustal strength, Na_2SO_4 will be the stable Na-bearing phase.

Discussion

To put the results in Figures 2-5 in perspective, it is important to note that available data indicate an outermost crust of Io (at least 0.1-1 km) composed primarily of SO_2 and elemental S with the Na-S phases and silicate materials being relatively minor constituents [*Smith et al.*, 1979; *Kieffer*, 1982]. Further, S and/or SO_2 must be buried by recycling to sufficiently high (PT) conditions to become the pressurized volatiles driving the extensive volcanic activity. Liquid SO_2 has a broad stability field, and it is inevitable that shallow crustal layers contain liquid SO_2 aquifers [*Kieffer*, 1982] and that SO_2 is a major phase to depths determined primarily by the strength of overlying crustal layers. These depths and the corresponding (PT) conditions will be subject to local geology and are likely to be highly variable. For purposes of illustration consider a range of local Iotherms ranging from 70 to 1000 K/km [*Kieffer*, 1982; *Matson et al.*, 1993] and a hydrostatic pressure gradient of 50 atm/km. For Iotherms less than 200 K/km the hydrostatic pressure is sufficient to contain $SO_2(l)$ down to the triple point (431 K). Even at 1000 K/km, the liquid SO_2 vapor pressure does not exceed the Iotherm until temperatures greater than 325 K. Thus 325 K is a reasonable estimate for the minimum temperature that SO_2 will reach during recycling. *McEwan and Soderblom* [1983] distinguish large ("plumes") and small ("fumaroles") active volcanic centers on Io and propose that the fumaroles are SO_2-driven whereas the plumes correspond to elemental S volcanoes. The fumaroles probably represent regions of lower than average heat flow located between major crustal silicate magmatic intrusions. The fumarolic environment is thus a SO_2-rich upper crust, corresponding to regions I and IIA (Figure 1), and in this region the equilibrium Na phase is Na_2SO_4 for either Na_2O or Na sulfides as input phases from the surface. The kinetics of reactions (1) and (2) in fumarolic regions might be slow; however it is likely that today's crustal recycling has been essentially the same for at least 10^9 years, making thermochemical equilibrium in region I on Io plausible even to temperatures as low as 300 K.

For regions with Iotherms less than 200 K/km or, in general, for regions of high crustal strength, it will be possible to contain SO_2 vapor in portions of the Io crust corresponding to region II (Figure 1). In these situations the SO_2 fluid pressure would greatly exceed the minimum required to be in the Na_2SO_4 stability field according to Figures 2-4. Regions of high crustal strength would most probably occur as a consequence of surface silicate lava flows or shallow intrusions [*Johnson et al.*, 1988] which bury surface SO_2 and S deposits. Figure 4 shows that if SO_2 pressures of 10-100 atmospheres can be contained, Na_2SO_4 will be the equilibrium phase all the way to silicate magmatic temperatures. Thus a large variety of crustal environments favor the conversion of Na_2S_x to Na_2SO_4.

However, silicate magmatic intrusions also create high-temperature regions, which as Figures 3-5 indicate, can favor the conversion of Na_2SO_4 to Na_2S_x, depending on whether SO_2 is contained or vented. The consequences of sudden heating of SO_2-S mixtures are model-dependent, but in general, if the heating is fast and accompanied by eruptive venting of both S and SO_2, it is possible that the fugacities of both species would remain in the Na_2SO_4 stability field. For example, as illustrated in Figure 5 for 1100 K, roughly $f(S_2)/f(SO_2) > 10^2$-10^3 is required to convert preexisting Na_2SO_4 to Na_2S_x. Although arbitrary, the 1100 K temperature illustrated in Figure 5 is plausible for large volumes surrounding silicate intrusions and flows and probably represents a rather common upper crustal temperature. In many cases, given the rapid timescales during venting, the prior Na phases will be quenched in, so that, e.g., if Na_2SO_4 were present or produced (region II) prior to venting, it would be preserved, independent of the details of the (PT) trajectories and of the effects of SO_2-S fractionation which is very likely to occur during eruption.

However, situations when SO_2 is preferentially degassed relative to S are also plausible; these favor Na_2S_x relative to Na_2SO_4. If a region is heated by an approaching silicate magmatic intrusion but initially remains unsealed relative to venting, SO_2 will preferentially be degassed first. Then, if the region is sealed, e.g., by being capped by a surface lava flow, temperatures can rise, and elemental S contained. To use a specific example based on Figure 5, if the region is heated to 1100 K after previous SO_2 degassing to produce $f(SO_2)/f(S_x) \leq 0.001$, then the region will lie within the Na_2S_x stability field. This specific example is arbitrary, but the conclusion is not highly sensitive to the chosen parameters, and events of this type seem plausible, e.g., convection in a liquid S lava lake would provide effective venting of SO_2, leading to Na_2S_x formation.

The plume source regions are the Io environments most closely corresponding to region III, for which both major upper crustal constituents are in the vapor phase. A long-lived plume will develop a local recycling system of crustal volatiles, which serves to transport the heat from a near-surface silicate magmatic intrusion. Given the large difference in volatility between SO_2 and elemental S, the evolution of this recycling system will relatively quickly produce a pure elemental S plume. This high-temperature, continually venting environment will produce Na_2S_x. A complication with this analysis is that, except possibly for transient explosive events, any Io crustal region which contains elemental S vapor, e.g., plume throats and source regions, must have a solid silicate "container." Thus the region III calculations which neglect any silicate interactions may be oversimplifications. It may be better to think of the plume source regions as a major site of primary Na extraction from silicate. If the gas phase in the plume source regions is predominantly elemental S, then the source regions may contain relatively large pools, mini magma chambers, of Na_2S_{x1} Recycling of S in plumes is the steady state situation, but occasionally an intense pulse of silicate magmatism will produce surface silicate lava flows which provides an opportunity for transfer of Na to the upper crust by Na volatilization or by interaction with S or SO_2.

Given that Na_2SO_4 is a very stable compound, my original expectation was that crustal recycling would produce only Na_2SO_4, yielding a clean, model-independent conclusion. Although in major regions of the Io crust, thermochemistry favors Na_2SO_4 formation, other regions which have been degassed of SO_2 relative to S will be locations where Na sulfides will be formed. Thus, even if Na sulfides are not the primary phase in which Na is initially brought to the Io surface (e.g., if mechanisms 1 and 4, discussed in the introduction, dominate), Na sulfides may be important phases on the present-day Io surface. Given the realistic view that a wide variety of crustal regimes will be present and that the thermochemical reaction products from all these regimes will be transported to the surface during eruptions, I conclude that the Io Na atmosphere has contributions from both Na_2SO_4 and Na-sulfides. This is not as tight a constraint as originally hoped, but a two-component mixture is still a relatively simple result. Although the

discussion of Na_2O destruction was presented, for simplicity, in terms of Na_2SO_4 production, in regions of low $f(SO_2)/f(S_2)$, Na_2S_x will be formed instead. If thermochemistry is dominant, only transient concentrations of Na_2O are possible on the Io surface, even if Na volatilization is the primary means of extracting Na from silicate magmas.

The proportions of Na_2SO_4 and sulfides depends on Io geology, but in turn, observational knowledge of the proportions can be a geological constraint. Such observations are possible; for example, it is likely that fast Na atoms in the Io torus are produced by dissociation of accelerated molecular ions [*Schneider et al.*, 1991]. The nature of these Na-bearing molecules is unknown at present, but the proportion of NaO to NaS molecules is a measure of the sulfate/sulfide surface mixing ratio. For example, if vented, high temperature (e.g., lava lake) environments are dominant, NaS molecules will be dominant Na-bearing species in the Io atmosphere.

A result of this study is that, contrary to general expectations, the Na mineralogy of the Io surface may have lost all record of the primary mechanisms (1-4, etc.) by which Na was extracted from silicate starting materials. Nevertheless, these mechanisms are important science issues because they are an important constraint on Io geologic processes and history, as well as a means, in principle, of identifying the types of silicate magmas involved. Even if the primary Na mineralogy has been destroyed by crustal recycling, the overall chemistry of the primary processes has not. Thus data, even good upper limits, on "minor" elements (K, Ca, Mg, Fe, etc.) in the Io atomic cloud or torus would be of great importance in advancing knowledge of both the geology and chemistry of Io [cf. *Johnson and Burnett*, 1993].

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